

Amendments to th Specification

Please amend the title as follows:

~~Materials and Methods for the Production and Purification of~~
~~Chlorofluorocarbons and Hydrofluorocarbons~~ Hydrogenation Processes

At p. 1, before "Field of the Invention", please insert the following

--CROSS REFERENCE TO RELATED APPLICATION

This application is a divisional of U.S. Application No. 09/966,158 filed on
September 28, 2001.

Please replace paragraph [0001] with the following rewritten paragraph:

[0001] The present invention is directed to ~~synthetic~~ production methods, as well as, synthetic and ~~physical~~ separation methods. More particularly, the present invention is directed to methods for ~~efficiently~~ manufacturing selective isomers of chlorofluorocarbons and hydrofluorocarbons from aliphatic, olefinic or partially halogenated hydrocarbons.

Please replace paragraph [0002] with the following rewritten paragraph:

[0002] Since the beginning of global warming concerns, chlorofluorocarbon manufacturers have had to produce compounds that perform substantially the same as fully halogenated chlorofluorocarbons without the adverse environmental impact. Only through the introduction of these new compounds have their environmental impact been completely understood. In certain instances, some of these new compounds have been removed from the marketplace. These types of issues make the flooding agent, ~~extinguishing~~ extinguishant, propellant and refrigerant production industry a dynamic and ever-changing marketplace where processes for the production of

chlorofluorocarbons and fluorocarbons are advancing quickly to accommodate both environmental as well as economical requirements.

Please replace paragraph [0016] with the following rewritten paragraph:

[0016] An additional process according to this invention provides for separating C-3 chlorofluorinated compounds from a halogenation reaction product. One embodiment of this invention includes the adjustment of a halogenation reaction product to a sufficient temperature to separate the reaction product into three ~~phases~~; phases: an upper gas phase and top and bottom liquid phases, wherein the upper gas phase contains primarily HCl, the top liquid phase contains HF and the bottom liquid phase contains essentially acid-free C-3 chlorofluorinated ~~compounds~~; compounds.

Please replace paragraph [0022] with the following rewritten paragraph:

[0022] Figure 3 is a block diagram of an embodiment of ~~Step I~~ according to the present invention.

Please replace paragraph [0023] with the following rewritten paragraph:

[0023] Figure 4 is a block diagram of an embodiment of ~~Step II~~ according to the present invention.

Please replace paragraph [0024] with the following rewritten paragraph:

[0024] Figure 5 is a block diagram of an embodiment of ~~Step III~~ according to the present invention.

Please replace paragraph [0025] with the following rewritten paragraph:

[0025] Figure 6 is a block diagram of an embodiment of ~~Step IV~~ according to the present invention.

Please replace paragraph [0026] with the following rewritten paragraph:

[0026] Figure 7 is a graphical representation of ~~the increased~~ catalyst life observed in according to an embodiment of ~~Step IV performed according to~~ the present invention.

Please replace paragraph [0027] with the following rewritten paragraph:

[0027] ~~For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended. The invention includes any alterations and further modifications in the illustrated devices and described methods and further applications as would be conveyed thereby to one skilled in the art to which the invention relates.~~ This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

Please replace paragraph [0028] with the following rewritten paragraph:

[0028] Referring now to **Fig. 1**, in one embodiment this invention provides processes for the production of chlorofluoropropanes and fluoropropanes from aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms. Other embodiments of this invention provide specific processes for ~~hydrodehalogenating~~ hydrodehalogenation, as well as, isomer and reaction product purification. Selected embodiments of this invention will be described in turn beginning with the broad chemical process steps used to produce selected chlorofluorocarbons and fluorocarbons.

Please replace paragraph [0031] with the following rewritten paragraph:

[0031] Referring now to Fig. 2, formation of excess amounts of CFC-216ba in ~~Step 4~~ during halogenation has been observed when the reaction is allowed to exotherm excessively. The large amounts of energy released during this exotherm are probably the ultimate reason for excess CFC-216ba isomer formation. When these types of conditions are allowed to prevail, ratios as low as 2:1 CFC-216aa:CFC-216ba can be observed in these early reaction streams.

Please replace paragraph [0032] with the following rewritten paragraph:

[0032] ~~During the course of the present invention, it was discovered that one~~
One way to control this phenomenon ~~was~~ can be to carefully operate the initial halogenations so as to avoid uncontrolled exotherms. The reactor used according to the present invention has the ability to use cool heat transfer oil and includes conventional chemical and engineering controls to insure suppression of exotherms. In another aspect of the present invention, HF can be replaced as the main diluent for the reaction. **Figs. 3-4** show a schematic flow diagram for a process according to the present invention that includes a two temperature zone chlorofluorination of a C-3 reactant selected from propane, propylene, partially halogenated C-3 acyclic hydrocarbons, and mixtures thereof, with hydrogen fluoride and chlorine in the presence of a chlorofluorination catalyst. The process is highly selective in the production of CFC-216aa, without the formation of any significant amount of FC-218 (0 to less than 0.5 percent by weight). The high yield and selectivity of the process of the present invention in the synthesis of CFC-216aa is very advantageous for the subsequent production of HFC-227ea as discussed below.

Please replace paragraph [0033] with the following rewritten paragraph:

[0033] The present invention provides, in one aspect, two step processes for efficiently producing CFC-216aa. The chemical steps ~~are~~ can include the sequential replacement of hydrogen with chlorine and the subsequent partial replacement of chlorine with fluorine atoms. Multiple products ~~are~~ may be formed with intermediate fluorinated materials being the majority. Careful temperature control ~~minimizes~~ may minimize by-product formation. Typical reaction products may include C-3 molecules with 2 to 7 fluorine atoms, the rest being chlorine. The cracking of the C-3 backbone to form C-1 and C-2 materials as undesired impurities ~~is also~~ has also been observed. According to one embodiment, the output of ~~Step I will~~ this reactor can be fed directly into ~~Step II~~ a subsequent reactor as shown in Fig. 4, which is run at a higher temperature.

Please replace paragraph [0034] with the following rewritten paragraph:

[0034] Individual reactants may be fed under flow control to vaporizer(s) 14, as shown in **Fig. 3**. The vaporized chlorine and HF are mixed and fed into a superheater of ~~Step I~~. It has been determined that careful mixing of the reactants and temperature regulation ~~helps~~ may help to control reaction exotherms and lack of control ~~leads~~ may lead to the formation of undesired by-products arising from cracking the C-3 backbone.

Please replace paragraph [0035] with the following rewritten paragraph:

[0035] The predominant reaction occurring in exemplary chlorofluorination Steps I and II ~~can~~ may be summarized, as follows, with high selectivity in the production of CFC-216aa:

Please replace paragraph [0036] with the following rewritten paragraph:

[0036] ~~The~~ According to one aspect, the process includes a first step₁ wherein C-3 reactants selected from the group consisting of aliphatic, olefinic or partially halogenated hydrocarbons having at least three carbon atoms are contacted with Cl₂ and HF in the presence of a metal containing catalyst. As illustrated in Fig. 3, this reaction is preferably performed in the gas phase by the careful mixing of C-3 reactants with a mixture of hydrogen fluoride (HF) and chlorine (Cl₂) in the presence of a metal containing catalyst at a sufficient temperature to form perhalogenated compounds.

Please replace paragraph [0037] with the following rewritten paragraph:

[0037] In one embodiment of the present invention, the C-3 reactant is selected from the group consisting of aliphatic, olefinic and/or partially halogenated ~~hydrocarbons~~ hydrocarbons. ~~The C-3 reactant may be premixed with a mixture of~~ hydrogen fluoride, and then mixed with chlorine before entering chlorofluorination reactor 16 containing a fixed bed of metal containing catalyst.

Please replace paragraph [0039] with the following rewritten paragraph:

[0039] According to one embodiment of the present invention, the HF and C-3 reactants are premixed before being combined with the chlorine gas and conveyed into a chlorofluorination reactor. It is preferred to premix (dilute) the C-3 reactant with the hydrogen fluoride reactant prior to combining the HF/C-3 gas reactants with the chlorine gas reactant in order to minimize the potential reaction of the C-3 reactant, e.g., propane and/or propylene with concentrated chlorine gas. Accordingly, at least one of the C-3 reactant or the chlorine, preferably both the C-3 reactant and chlorine, ~~should~~ may be diluted with hydrogen fluoride prior to combining the C-3 reactant with the chlorine gas.

Please replace paragraph [0041] with the following rewritten paragraph:

[0041] The ~~chlorination~~ halogenation of aliphatic, olefinic, or partially halogenated hydrocarbons having at least three carbon atoms is a highly exothermic reaction which may be controlled through the use of excess quantities of hydrogen fluoride, a diluent, or a an external heat transfer medium together or in combination, to absorb the heat evolved and to maintain temperature control of the mixture.

Please replace paragraph [0042] with the following rewritten paragraph:

[0042] To reduce the impact of exotherms, preferably, a stoichiometric excess of hydrogen fluoride ~~is~~ may be maintained in order to minimize decomposition of the C-3 reactant to C-1 and C-2 by-products, and the formation of the less desired ~~CFC-216ba~~, preferably CFC-216ba. Preferably, about 6 to about 64 moles of HF per mole of C-3 reactant may be utilized. It is preferred to provide an excess of chlorine gas as well, preferably about 8 to about 10 moles of Cl_2 per mole of C-3 ~~reactant, but~~ reactant. However, an excess of Cl_2 is not required. In a preferred embodiment, the ratio of Cl_2 to C-3 reactants can be about 8.2:1. The molar ratio of HF to Cl_2 ~~is~~ may be from about 0.75:1 to about 8:1. ~~Perferably~~, Preferably, the molar ratio of HF to Cl_2 ~~is~~ may be about 4:1. Moreover, in another embodiment, a diluent may be added to the reaction to decrease undesired isomer and formation of cracking materials.

Please replace paragraph [0043] with the following rewritten paragraph:

[0043] Preferably, the chlorofluorination reactor 16 used to perform this invention ~~is~~ may be maintained at a reaction pressure of about 0 psig to about 750 psig, preferably about 0 psig to about 750 psig and at a temperature in the range of about 150°C to about 450°C, and preferably about 220°C. ~~For best results, residence~~
Residence time in chlorofluorination reactor 16 ~~should~~ may be in the range of about 0.5

seconds to about 30 seconds and preferably about 5 to about 10 seconds. The resulting An exemplary reaction mixture ~~coming out of exiting~~ Step I shown in **Fig. 3** is rich in $C_3Cl_4F_4$ and $C_3Cl_3F_5$, but ~~will~~ may also contain CFC-216aa and many other under fluorinated compounds. ~~Preferably,~~ In an exemplary aspect, reaction products of this first step are conveyed directly to Step II, as shown in **Fig. 4**, ~~however,~~ Fig. 4. However, it is recognized that the reaction products of Step I, as shown in **Fig. 3**, may be further purified or supplemented prior to continuing on to Step II. A main goal in Step II is can be the selective fluorination of ~~these~~ under-fluorinated compounds to the desired isomer CFC-216aa.

Please replace paragraph [0044] with the following rewritten paragraph:

[0044] The In the illustrated embodiment, the second step in this process may ~~replaces~~ replace all of the terminal chlorine substituents with fluorine to produce CFC-216aa. According to one aspect of the present invention, this is accomplished through the use of one or more of high temperature reaction conditions, excess HF, and a metal containing catalyst.

Please replace paragraph [0045] with the following rewritten paragraph:

[0045] As shown in **Fig. 4**, the Step I reaction stream is directly fed into a superheater 24. Optimally, this stream is then fed to Step II reactor 26. Again, as before in Step I, careful temperature regulation is can be used to control the reaction.

Please replace paragraph [0046] with the following rewritten paragraph:

[0046] The second reaction can take place either in the same reactor as exemplary Step I or, preferably, in a second reactor. The second ~~step is~~ reaction can be carried out at a higher temperature than the first ~~step~~ reaction with a stoichiometric

excess of hydrogen fluoride. According to one embodiment, a stoichiometric excess of chlorine can be used to ensure chlorofluorination of the ~~Step I~~ first reaction products.

Please replace paragraph [0047] with the following rewritten paragraph:

[0047] ~~Preferably, Step II reactor~~ Reactor 26 is ~~is~~ can be a fixed-bed reactor having a metal containing catalyst, maintained at a reaction pressure of about 0 psig to about 750 psig and preferably about 100 psig, and at a temperature higher than the temperature required in exemplary Step I. Step II ~~occurs~~ may occur at a temperature ranging from about 300°C to about 550°C, and preferably at about 470°C. It is preferred that the molar ratio of reactants in Step II, should be maintained at about 6 to about 64 moles of hydrogen fluoride per mole of perhalogenated compounds. As in Step I, the source and quality of anhydrous HF used in Step II is not critical. It is to be understood by those skilled in the art that anhydrous, recycled, and/or differing grades of HF can be used in Step II. As in Step I, a diluent may be added to control exotherms and increase isomeric yield.

Please replace paragraph [0057] with the following rewritten paragraph:

[0057] Generally, all fluorination catalyst ~~were~~ can be prepared by mixing appropriate amounts of the selected metal salt and support (if necessary) in DI Water. This mixture ~~is~~ may be allowed to stand for approximately 0.5 hour and the excess water ~~is~~ can be filtered off by vacuum filtration. The resulting solid ~~is~~ may then ~~be~~ dried overnight in a gravity oven at 115°C and then charged to the reaction tubes ~~were~~ where it ~~is~~ can be further dried at 150°C with a inert gas purge and then activated with HF before the reaction feeds are started.

Please replace paragraph [0090] with the following rewritten paragraph:

[0090] As this example demonstrates the organic phase, once separated according to an embodiment of the present invention, is essentially ~~acid-free~~ acid-free. This allows for the immediate isolation of specific chlorofluorination reaction products without the need for costly and inefficient distillation. Moreover, Table 7 demonstrates that other halogenated organics can be separated from HF₁ according to the present invention. These chlorofluorination reaction products can be isolated₁ according to another process of the present invention as herein described next.

Please replace paragraph [00136] with the following rewritten paragraph:

[00136] In accordance with still another process of the present invention, a halogenated organic compound is provided to be contacted with H₂ and a catalyst to form a hydrodehalogenation reaction product. In a preferred embodiment₁ the halogenated organic compounds are the Step III reaction products which include CFC-217ba. Accordingly, the halogenated organic compounds are premixed with hydrogen and contacted with a metal containing catalyst at sufficient temperature to produce a hydrodehalogenation reaction product. In still another embodiment₁ the hydrodehalogenation reaction products include HFC-227ea. A reaction of this embodiment is shown below:

